DYNAMICS OF NITRO-NITRITE REARRANGMENT IN NITROMETHANE RADICAL CATION

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Nitromethane, the smallest organic-nitro compound, is commonly studied to model ignition and detonation of energetic materials. Using pump-probe femtosecond laser photoionization mass spectroscopy, coupled-cluster theory, and ab initio molecular dynamics, we study nitromethane cation (NM^+) fragmentation into CH_3^+, NO_2^+, and NO^+. From theoretical analysis, NO_2^+ and CH_3^+ are formed through direct cleavage of the C-N bond, whereas NO^+ forms spontaneously upon nitro-nitrite rearrangement (NNR) of the NM^+ cation. Direct ionization into the electronically excited D_1 or D_2 states by the pump pulse provides sufficient excess energy to initiate the NNR pathway. With excess energy stored in the NNR transition state, molecular dynamics simulations indicate that NNR requires 660 ± 230 fs and is typically followed by rapid NO^+ loss 100-200 fs later. Experimentally, the fragmentation pathways to NO^+ and CH_3^+ are in competition, with associated decay timescale of $\sim 480 \pm 200$ fs that is similar to the computed NNR timescale. This result suggests that CH_3^+ is formed by further excitation of the NM^+ initially ionized into the D_1 or D_2 states before it undergoes NNR. Finally, the dissociation to NO_2^+ from NM^+ can be assigned to a $D_0 \rightarrow D_2$ transition.